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16. ABSTRACT

Numerous unidentified oil samples collected from the surface waters of the United States were analyzed by the method of ratios of infrared absorbance, using six wavenumbers. Two key ratios, 810 cm^{-1}/1735 cm^{-1}, $^{-1}$and 810 cm^{-1}/720 cm^{-1}, were useful for the initial classification of the oil spill samples of unknown and uncharacterized origin, while confirmation requires the use of the other ratios. For rapid field evaluation, the graphic method is useful for classifying petroleum pollutants in water. Ratio values from unidentified petroleum pollutants are compared with those from industrial asphalts and residual fuel oils. Classical analyses--API gravity, solubility, boiling points, etc.--supplement the findings of the RI method. Asphalts, No. 6 fuel oils, No. 5 fuel oils, and a lubricating oil were characterized.

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Characterization of Oil Slicks on Surface Waters

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Numerous unidentified oil samples collected from the surface waters of the United States were analyzed by the method of ratios of infrared absorbance, using six wavenumbers. Two key ratios, 810 cm^{-1}/1375 cm^{-1}, and 810 cm^{-1}/720 cm^{-1}, were useful for the initial classification of the oil spill samples of unknown and uncharacterized origin, while confirmation requires the use of the other ratios. For rapid field evaluation, the graphic method is useful for classifying petroleum pollutants in water. Ratio values from unidentified petroleum pollutants are compared with those from industrial asphalts and residual fuel oils. Classical analyses—API gravity, solubility, boiling points, etc.—supplement the findings of the RIA method. Asphalts, No. 6 fuel oils, No. 5 fuel oils, and a lubricating oil were characterized.

Petroleum products damage natural recreational facilities and contribute taste and odor problems in potable water and fish products. As the demand for petroleum products becomes greater and ocean oil transports become larger, oil spills will become more frequent. Oil spills usually occur without eye witnesses. In such cases, technical information and data are necessary to facilitate location and identification of the sources responsible for the water pollution created. Following identification, control procedures may be properly enforced.

Johnson *et al.* (1968) and Kawahara (1969a) reported a rapid procedure for the characterization of heavy oils and asphalts. This procedure, developed for industrial heavy oils and asphalts, characterized well the big Chicago oil spill into Lake Michigan in 1967. The present paper is an elaborate extension of the procedure, relating the

Table I. Ratios of Infrared Absorbances of Commercial Asphalts and Heavy Residual Oils

Asphalts	720Cm $^{-1}$/1375 Cm $^{-1}$	3050 Cm $^{-1}$/2925 Cm $^{-1}$	810 Cm $^{-1}$/1375 Cm $^{-1}$	810 Cm $^{-1}$/720 Cm $^{-1}$	1600 Cm $^{-1}$/1375 Cm $^{-1}$	1600 Cm $^{-1}$/720 Cm $^{-1}$
30B	0.36	0.27	0.23	0.65	0.53	1.47
24A	0.30	0.18	0.20	0.67	0.58	1.90
17B	0.30	0.25	0.20	0.67	0.40	1.37
13A	0.35	0.24	0.24	0.67	0.29	1.65
29B	0.28	0.22	0.21	0.75	0.53	1.90
31B	0.29	0.21	0.21	0.76	0.49	1.66
36B	0.32	0.28	0.21	0.80	0.49	1.52
23A	0.30	0.23	0.25	0.84	0.70	2.37
29A	0.32	0.27	0.28	0.86	0.59	1.78
28B	0.31	0.19	0.24	0.89	0.66	2.12
35B	0.26	0.24	0.24	0.94	0.55	2.13
36A	0.26	0.24	0.25	0.95	0.59	2.33
19B	0.25	0.16	0.25	0.98	0.40	1.59
22B	0.26	0.23	0.26	0.99	0.67	2.57
18A	0.21	0.20	0.22	1.08	0.40	1.92
30A	0.26	0.25	0.29	1.14	0.60	2.30
23B	0.21	0.21	0.25	1.22	0.59	2.85
19A	0.28	0.23	0.34	1.25	0.59	2.06
24B	0.19	0.18	0.24	1.26	0.58	3.11
31A	0.28	0.17	0.38	1.34	0.65	2.33
Av.	0.28 ± 0.03	0.22 ± 0.03	0.25 ± 0.03	0.94 ± 0.18	0.54 ± 0.08	2.05 ± 0.37
Heavy Residual Oils						
15B	0.29	0.23	0.27	0.90	0.34	1.14
13B	0.24	0.18	0.23	0.93	0.35	1.46
22A	0.26	0.30	0.30	1.31	0.55	2.15
14A	0.15	0.21	0.20	1.34	0.33	2.21
15A	0.16	0.22	0.22	1.40	0.35	2.20
16B	0.18	0.26	0.24	1.40	0.46	2.67
20A	0.24	0.19	0.34	1.41	0.46	1.92
27A	0.31	0.32	0.45	1.42	0.64	2.05
17A	0.16	0.23	0.24	1.50	0.45	2.85
14B	0.17	0.25	0.27	1.54	0.47	2.69
20B	0.23	0.30	0.35	1.55	0.51	2.24
27B	0.16	0.21	0.29	1.86	0.50	3.27
28A	0.22	0.32	0.51	2.37	0.75	3.51
12A	0.23	0.38	0.57	2.52	0.84	3.47
16A	0.21	0.37	0.54	2.59	0.88	4.18
11B	0.21	0.29	0.59	2.80	0.73	3.48
12B	0.20	0.37	0.60	2.97	0.76	3.78
21B	0.13	0.34	0.46	3.79	0.62	5.05
26A	0.16	0.25	0.59	3.93	0.83	5.54
25B	0.14	0.31	0.56	4.08	0.90	6.47
26B	0.13	0.25	0.56	4.24	0.83	6.37
Av.	0.20 ± 0.04	0.28 ± 0.05	0.40 ± 0.14	2.18 ± 0.92	0.60 ± 0.17	3.27 ± 1.18

utility of the ratio-of-infrared-absorbance (RIA) method on numerous oil spills of unknown character in the inland and coastal waters of the United States. Additional tests (Kawahara, 1969b) confirm the findings disclosed by the infrared method.

Objective

The objective was to use the newly developed method to test for unidentified oil pollutants found in surface waters and to confirm the characterization findings with data provided by classical methods.

Experimental

Extraction. Although conditions of samples were varied, all were extracted with chloroform; the extract was then filtered through anhydrous sodium sulfate.

Concentration and Drying. The concentrate was obtained in the manner described previously. All samples were dried at 40° C/0.5 mm for 1 hour. Drying of the sample at 90° C/0.2 mm causes distillation of the low boiling components of No. 1 or 2 fuel oil. Distillates were examined for products other than chloroform.

Infrared Absorption Spectra. Specimens were prepared for analyses as described previously. Hard, viscous materials were warmed and transferred with aid of a spatula or transferred as a concentrated chloroform solution that was dried under the infrared lamp for 15 minutes at 75° C. Soft, nontacky materials were transferred with aid of a spatula. The thickness of the film was adjusted so that the transmission readings varied from 80 to 98% of the full scale at 2925 cm $^{-1}$.

Discussion

In Table I, the ratios of infrared absorbances of 20 commercial asphalts (not diluted with solvent) are shown, with the ratios of infrared absorbances of 21 commercial heavy residual oils. The differences in values between the asphalt and the heavy residual oil lie in the 810 cm $^{-1}$/1375 cm $^{-1}$, 810 cm $^{-1}$/720 cm $^{-1}$, and 1600 cm $^{-1}$/720 cm $^{-1}$ ratios.

The strongest defining ratio is 810 cm $^{-1}$/720 cm $^{-1}$. For this ratio, the asphaltic materials have smaller values or less material that is responsible for the absorption at 810 cm $^{-1}$. Furthermore, the asphalts appear to show strong

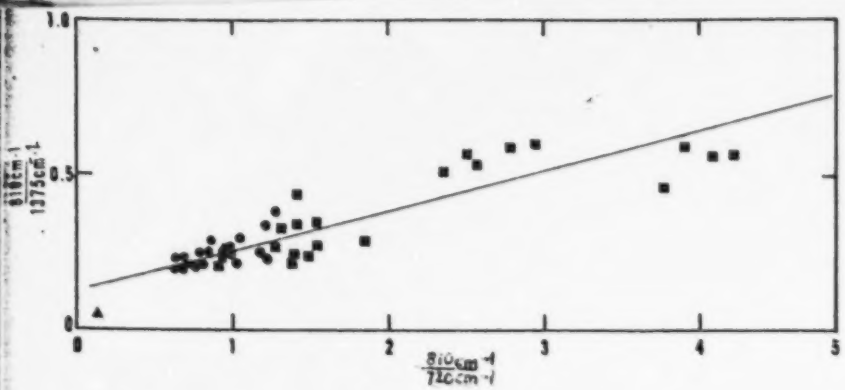

Figure 1. Linear relationship of commercial asphalts and No. 6 fuel oils involving two ratios of infrared absorbance

▲ Lubricant oil
■ Heavy residual oil
● Asphalt

ger absorption at 720 cm $^{-1}$. For the 810 cm $^{-1}$/720 cm $^{-1}$ ratio in asphalt, the values range from 0.65 to 1.34; the mean deviation for the 20 asphalt samples is 0.94 ± 0.18. For the 21 heavy residual oils, the values range from 0.90 to 4.24; the mean deviation is 2.18 ± 0.92. With the use of the mean deviation calculations, the upper limit for asphalts is determined to be 1.12 and the lower limit for the heavy residual oil is 1.26. The generalized overlap for asphalt and heavy residual oil is not a mathematical problem for the 810 cm $^{-1}$/720 cm $^{-1}$ ratio. However, of the 41 samples listed, the RIA method does not resolve the last five asphalt samples and the first two heavy residual oil samples. Samples tested in this overlap region require additional examination for clarification.

The two key ratios, 810 cm $^{-1}$/720 cm $^{-1}$ and 810 cm $^{-1}$/1375 cm $^{-1}$, of 41 commercial products manufactured by seven petroleum companies determined ratio points located along the line $Y = 0.13X + 0.13$, as shown in Figure 1. All values were averaged from four spectra obtained by using four different and limited thicknesses per sample.

As shown in Figure 1, the 20 commercial asphalt samples are represented by values clustered between 0.6 and 1.3 for the 810 cm $^{-1}$/720 cm $^{-1}$ ratio, while their 810 cm $^{-1}$/1375 cm $^{-1}$ ratio varied between 0.2 and 0.4. Heavy residual oils tested lie at points greater than 1.30 for the value of the 810 cm $^{-1}$/720 cm $^{-1}$ ratio, except for two samples of the 21 oils tested. At the boundary between the ranges of ratio points defining asphalt and heavy residual fuel oil for the 810 cm $^{-1}$/720 cm $^{-1}$ ratio lie two points somewhat beyond their defining values. Heavy residual fuel oils may, to a small extent, approach asphalt in properties, as both are produced in the final stages of processing crude oils; this may explain, in part, the overlap in the asphalts and the heavy residual oils.

Approximately one half of the heavy residual oils are located between 0.2 and 0.4 for the 810 cm $^{-1}$/1375 cm $^{-1}$ ratio; the remainder have values greater than 0.4. This latter group of heavy residual oils also is characterized by values of 2.0 or greater for the 810 cm $^{-1}$/720 cm $^{-1}$ ratio. Five points designating heavy residual fuel oil and located in the center of the figure are derived from five midcontinent crude sources utilized by three companies. Examination of ratio values from samples 28A, 12A, 16A, 11B, and 12B showed a similar trend. Apparently, the producing source or horizon is one of the factors governing

Table II. Ratios of Infrared Absorbances of Unknown Oil Slicks

Oil Slick	720 Cm $^{-1}$/ 1375 Cm $^{-1}$	3050 Cm $^{-1}$/ 2925 Cm $^{-1}$	810 Cm $^{-1}$/ 1375 Cm $^{-1}$	810 Cm $^{-1}$/ 720 Cm $^{-1}$	1600 Cm $^{-1}$/ 1375 Cm $^{-1}$	1600 Cm $^{-1}$/ 720 Cm $^{-1}$	Classification Unknown
Allegheny R.	0.23	0.16	0.22	0.99	0.69	2.76	Asphalt
Ohio R-Miami R	0.20	0.20	0.23	1.15	0.64	3.21	Asphalt
Arthur Kill	0.31	0.30	0.29	0.93	0.50	1.57	Asphalt
40A B-D	0.27	0.33	0.26	0.97	0.36	1.32	Asphalt
49A B-E	0.25	0.27	0.24	0.99	0.33	1.33	Asphalt
39A B-B	0.25	0.28	0.25	1.01	0.35	1.41	Asphalt
45B B-O	0.12	0.28	0.28	1.28	0.44	2.00	Heavy residual fuel oil
38B B-H	0.15	0.25	0.21	1.29	0.48	3.02	HRFO
Baltimore	0.24	0.30	0.33	1.41	0.57	2.43	HRFO
Presque Island	0.23	0.30	0.33	1.43	0.62	2.66	HRFO
Charlottesville	0.13	0.21	0.22	1.69	0.43	3.21	HRFO
40B B-G	0.13	0.30	0.20	1.70	0.50	3.33	HRFO
51B B-I	0.15	0.25	0.29	1.86	0.49	3.18	HRFO
45A B-P	0.12	0.22	0.23	1.99	0.41	3.51	HRFO
Vicksburg	0.16	0.23	0.32	1.99	0.65	4.09	HRFO
Westchester Ck.	0.12	0.25	0.21	2.00	0.26	2.37	HRFO
43A B-M	0.12	0.23	0.24	2.09	0.41	3.52	HRFO
44B B-N	0.10	0.22	0.22	2.39	0.36	3.78	HRFO
Honolulu Pier 4	0.13	0.41	0.52	4.16	1.15	9.26	HRFO
Ala Moana	0.13	0.38	0.52	4.24	1.23	9.88	HRFO
Honolulu 2	0.11	0.40	0.49	4.48	1.15	10.55	HRFO
Ohio R, m. 479.2	0.14	0.31	0.64	4.54	0.63	4.49	No. 5 fuel oil

the amount of specific aromatics that absorb at 810 cm^{-1} in residual oils.

The location and wide dispersion of the points on the plot of 810 cm^{-1}/1375 cm^{-1} vs. 810 cm^{-1}/720 cm^{-1} suggest that this ratio method may be useful not only for the characterizaton of the residual fuel oil product but also for its identification if a mixture is not involved or may be resolved satisfactorily into single manufactured petroleum products. Presumably, the ratio points of asphalts are clustered, since these products are usually residues remaining after the final stages of processing crudes into marketable products. Severity of processing conditions in the final steps of manufacturing may tend to cause normalization of the two ratio parameters of the distillation residues.

Table II shows the RIA values calculated for some of the unidentified oil spill samples collected from surface waters during the past year. Inspection of the 810 cm^{-1}/1375 cm^{-1} and 810 cm^{-1}/720 cm^{-1} ratios reveals notable differences in magnitude for unknowns classified as asphalt and those classified as No. 6 fuel oil. The amount of aromatics that absorb at 810 cm^{-1} is relatively larger for the oil slicks classified as No. 6 fuel oil. A few No. 5 residual oils were analyzed. Compared to the No. 6 fuel oil, a similar trend is noted but with much larger 810 cm^{-1}/1375 cm^{-1} and 810 cm^{-1}/720 cm^{-1} ratios.

Six unidentified oil spills, classified as asphalt by the RIA method using 810 cm^{-1}/1375 cm^{-1} and 810 cm^{-1}/720 cm^{-1} ratios, have values fairly close to the two ratios established from the averages involving 20 commercial asphalt samples. Fifteen oil slicks of unknown origin and classified as heavy residual fuel oil, No. 6, have expectedly much larger values for ratio 810 cm^{-1}/720 cm^{-1} than the averages indicated for the asphalt. As the heavy residual fuel oil points of Figure 1 are widely scattered in contrast to the asphaltic points, the ratio points of the nonasphaltic unknowns are not expected to be identical to the averages of the six ratios found from 20 commercial heavy residual fuel oils. The distribution of the points for the unknowns, classified as No. 6 fuel oil, simulate the pattern of dispersion of points characteristic for commercially known No. 6 fuel oils.

For the 25 unidentified oil slicks, Figure 2 illustrates the graphical location of the two key RIA values on the $Y = 0.13X + 0.13$ experimental plot.

The six oil slicks of unknown origin and classified as asphalt lie very close to the $Y = 0.13X + 0.13$ plot established by the 41 commercial asphalt and No. 6 fuel oils. The 810 cm^{-1}/1375 cm^{-1} ratio of the asphaltic unknowns is between the limits of 0.20 and 0.35. For the 810 cm^{-1}/720 cm^{-1} ratio of the asphaltic unknowns, the boundary limits are 0.80 to 1.20. This quadrangular enclosure of the six unknowns, classified as asphalts, is within the limits established experimentally for the 20 commercial asphalt samples.

Table III. Ratios of Infrared Absorbances of Lubricating Oils, Known-Unknowns

	Motor Oil	53A	53B	42A
720 cm^{-1} / 1375 cm^{-1}	0.48	0.52	0.60	0.17
3050 cm^{-1} / 2925 cm^{-1}	0.20	0.28	0.24	0.25
810 cm^{-1} / 1375 cm^{-1}	0.06	0.08	0.05	0.12
810 cm^{-1} / 720 cm^{-1}	0.12	0.15	0.09	0.68
1600 cm^{-1} / 1375 cm^{-1}	0.11	0.13	0.24	0.20
1600 cm^{-1} / 720 cm^{-1}	0.24	0.25	0.40	1.26

Fifteen oil slicks of Figure 2 are classified as No. 6 fuel oil type, using the two key RIA values. These unknowns, in contrast to the asphaltic unknowns, are located somewhat below the experimentally determined line $Y = 0.13X + 0.13$ for the asphalt–No. 6 fuel oil relationship involving the 810 cm^{-1}/1375 cm^{-1} and 810 cm^{-1}/720 cm^{-1} ratios. Losses in the aromatics that are responsible for the absorption at 810 cm^{-1} are assumed to be responsible for the location of the points, classified as No. 6 fuel oil, below the commercial plot. Losses of the specified aromatics are assumed to be due to volatilization, autoxidation, and biogradation. The oxidized products—alcohols, aldehydes, and acids—can be solubilized in water.

The asphaltic unknowns, being more viscous, limit the area of surface contact with water. These may be less prone to evaporation and biodegradative reactions. Fast degradation and evaporation are presumed to occur for the heavy oil-water system that exposes greater surface area during liquid-liquid contact.

Several oil slicks were identified as lubricants by the use of the RIA method. Table III shows two unknowns (53A and 53B) which display unusually high specific paraffinic nature.

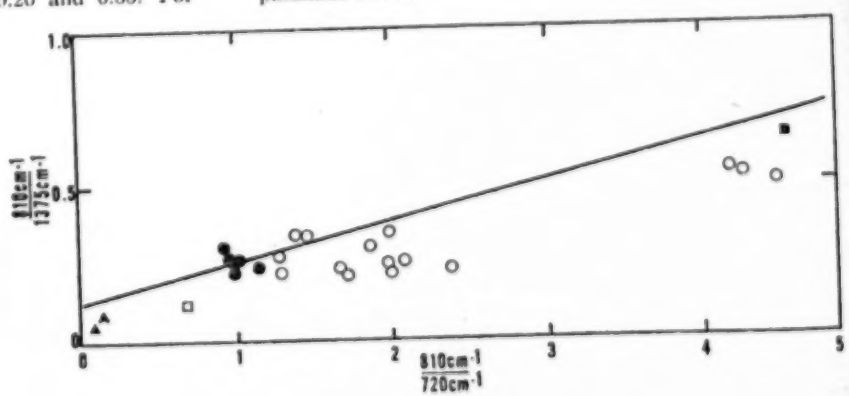

Figure 2. Ratios of infrared absorbance of oil spill samples of unknown origin

▲ Lubricating oil
● Asphalt
○ No. 6 oil
■ No. 5 oil
□ Lubricating-fuel oil

Table IV. Supporting Data for Characterization

Oil Slick	RIA	API Gravity	Solubility[a]			Infrared spectra
			Hexane	Ether	Chloroform	
45A B-P	HRFO 6	17	I	I	S	
43A B-M	HRFO 6	15	I	I	S	
44B B-N	HRFO 6	15	I	I	S	
45B B-O	HRFO 6	13	I	I	S	
38B B-H	HRFO 6	18	I	I	S	
53B B-J	Lube oil	27	S	S	S	Lube oil
42A[b] R-S	Mix	24	S	S	S	Lube oil + FO
53A GOW	Lube oil	32	S	S	S	Lube oil
44A DES	FO 5 or 6	17	I	I	S	FO 5

[a] I = insoluble, S = soluble. [b] Contains iron, lead, and zinc in large quantities.

Table V. RIA Values of Motor Oil, Asphalt, No. 5 Fuel Oil, and No. 6 Fuel Oil

	720 Cm^{-1}/ 1375 Cm^{-1}	3050 Cm^{-1}/ 2925 Cm^{-1}	810 Cm^{-1}/ 1375 Cm^{-1}	810 Cm^{-1}/ 720 Cm^{-1}	1600 Cm^{-1}/ 1375 Cm^{-1}	1600 Cm^{-1}/ 720 Cm^{-1}	Class.
Unknown 44A	0.14	0.31	0.64	4.54	0.63	4.49	No. 5
Unknown 44B	0.10	0.22	0.22	2.39	0.36	3.78	No. 6
Known average	0.20	0.28	0.40	2.18	0.60	3.27	No. 6
Known average	0.28	0.22	0.25	0.94	0.54	2.05	Asphalt
Known lube	0.48	0.20	0.06	0.12	0.11	0.24	Motor oil
Unknown 53A	0.52	0.28	0.08	0.15	0.13	0.25	Lube oil
Unknown 42A	0.17	0.25	0.12	0.68	0.20	1.26	Lube mix

The commercial motor oil sample exhibits similar ratios. Oil slicks of unknown origin (53A and 53B) correspond closely to the commercial lubricating oil with respect to the two key RIA values. Thus 53A and 53B are lubricating oils.

Ratio values of oil slick 42A indicate properties identifying it as a heavy fuel oil. However, a plot of the 810 cm^{-1}/720 cm^{-1} and 810 cm^{-1}/1375 cm^{-1} ratios shows that the 42A sample is intermediate between the known motor oil and the commercial asphalt points. Unknown 42A appears to be a mixture of lubricating oil and fuel oil.

To confirm findings revealed by the ratio of infrared absorbance method, other tests were used as shown in Table IV—for example, the RIA method showed Pacific Northwest sample 90B-N to be a No. 6 fuel oil. Table V shows the RIA values of oil slick 44B, B-N, to be slightly variant from the averages of industrial No. 6 fuel oils. The product appears to be No. 6 fuel oil with some asphaltic properties.

The solubility behavior test of oil sample 44B, B-N, suggests that the product is asphalt, grease, or heavy residual fuel oil. Its API gravity value is 15.2, which indicates a heavy residual fuel oil, asphalt, or grease. Grease, No. 4, and No. 5 fuel oils are eliminated since the spectrum of the unknown is unlike any of these. The oil slick is therefore No. 6 fuel oil with some asphaltic properties.

A recent oil spill on the Ohio River was investigated by the Ohio Basin Region Office personnel of the Federal Water Quality Administration. Solubility behavior test of a sample from this oil spill (44A) suggested that the product could be asphalt, grease, or heavy residual fuel oil. Interpretation of the infrared spectrum suggested that it was No. 5 fuel oil. As the API gravity was 16.9, lubricants and light fuel oils were eliminated as possibilities. Asphalt, No. 6 fuel oil, and grease were eliminated by the absence of certain infrared characteristics. The infrared pattern of the unknown was similar to several infrared patterns of No. 5 fuel oils. The oil slick was therefore No. 5 fuel oil. The infrared spectra of oil spill 44A and an authentic heavy residual fuel oil No. 5 are shown in Figure 3.

A sample (53A) of an oil spill in Gowan's Bay was collected recently by the FWQA's Hudson-Delaware Basins Office personnel. The spectrum and RIA values

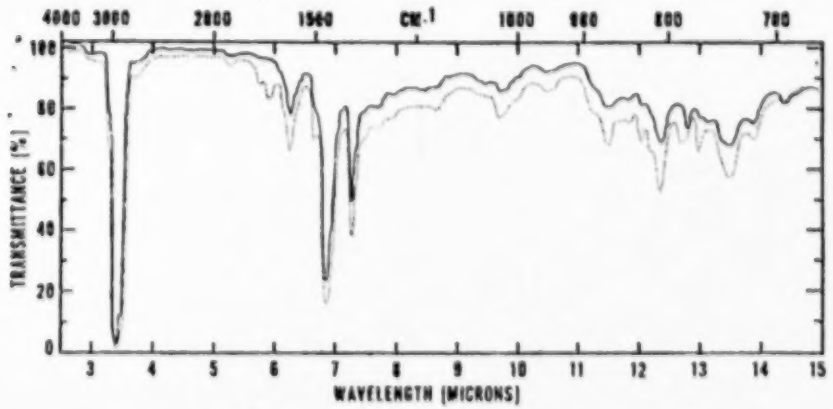

Figure 3. Infrared spectra of samples of oil spill and commercial fuel oil
···· Sample 44A, oil spill on Ohio River
—— Sample 54B, commercial fuel oil

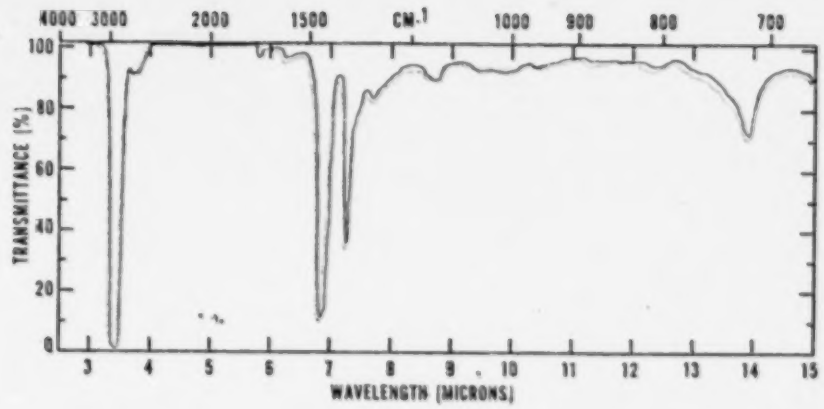

Figure 4. Infrared spectra of oil slick and motor oil
— Sample 54A, commercial SAE 50 motor oil
· · · Sample 53A slick of unknown origin, Gowan's Bay, N. Y.

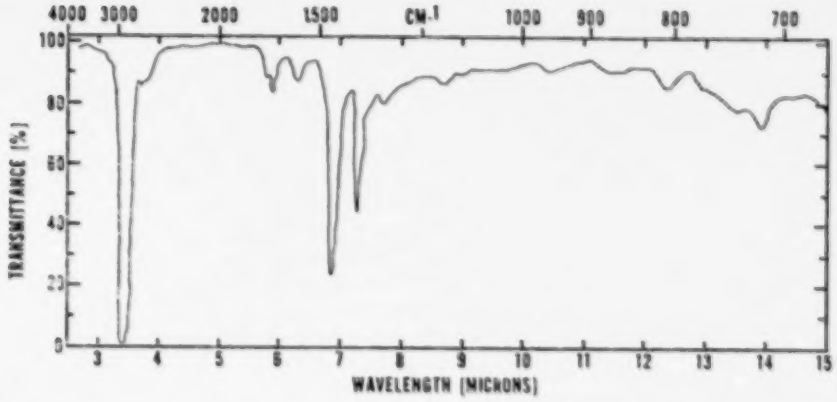

Figure 5. Infrared spectrum of sample of oil spill on Cuyahoga River at industrial outfall

revealed that 53A is a lubricating oil (Table V). The solubility behavior test of this oil spill sample suggested that the product was a material other than No. 5 fuel oil, No. 6 fuel oil, grease, or asphalt. Solubility results suggested that it might be a lubricating oil. The specific gravity was 31.5. As lubricating oil, white oil, and turbine oil have a specific gravity varying from 24 to 32, the oil slick was a type of lubricating oil. The infrared spectra of 53A and an authentic motor oil, SAE 50 premium nondetergent product, are shown in Figure 4.

A Cuyahoga River oil spill sample (42A) was shown by the RIA method to be a mixture of a lubricating oil and a fuel oil. Its two key RIA values determined a point on the $Y = 0.13X + 0.13$ line between a commercial motor oil and asphaltic–No. 6 fuel oil points.

The solubility behavior of this oil suggested the product to be other than grease, heavy residual oil, or asphalt. This oil slick was soluble in hexane, ether, and chloroform. The specific gravity was found to be 24.1, a value within the limits characteristic of a lubricating oil. Metal analyses revealed the presence of iron, lead, and zinc in unusually large amounts. It appeared to be a lubricating oil–fuel oil product used by a steel company. Figure 5 shows the infrared spectrum of 42A.

Rather than using the results obtained by classical methods as corroborative data, the approach to the characterization of the oil product may be to determine first the solubility of the dried oil slick. A specific gravity reading and/or distillation points obtained by gas chromatography (Worman and Green, 1965) or by classical methods are also helpful. Results of these tests can eliminate about one half to three fourths of the search time, as a large number of the petroleum products are eliminated from further consideration. Infrared data will generally lead to a specific characterization of the petroleum product.

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